Chin.J.Geochem.(2011)30:033–039
DOI: 10.1007/s11631-011-0484-8

Geochemical assessment of a siliceous limestone sample for cement making

Rao D.S.*, Vijayakumar T.V., Prabhakar S., and Bhaskar Raju G.

National Metallurgical Laboratory-Madras Centre CSIR Madras Complex, Taramani, Chennai-600 113, India

* *Corresponding author. E-mail: nmldsr@yahoo.co.in*

Received January 20, 2010; accepted March 1, 2010

Abstract A low grade siliceous limestone sample from the Jayantipuram mine of Andhra Pradesh, India, has been investigated for its suitability for cement making. Petrological as well as X-ray diffraction pattern studies indicated that the limestone sample was crystalline and dominantly composed of calcite and quartz. They are simple in mineralogy, and yet they have variable silica and lime contents. Geochemical analysis results of twenty five hand picked samples indicated that the limestone from the Jayantipuram mine shows a wide range of variations in LOI (29.94% to 40.64%), SiO_2 (6.14% to 27.18%), CaO (37.93% to 50.78%), Al_2O_3 (0.49% to 2.27%) and Fe_2O_3 (0.28% to 2.4%). MgO, K_2O, Na_2O, TiO_2 and MnO_2 are present in traces. CaO with LOI shows a strong positive correlation where as CaO with SiO_2 shows a strong negative correlation because of mineralogical factors. The chemical composition of the limestone reflects its mineralogical composition. The distribution of various elements in the acid-soluble fraction has been studied by the factor analysis method in order to interpret in terms of their mineralogy, sedimentary environment and diagenesis. Mineralogy, recrystallization and other diagenetic changes are the main factors affecting the distribution of the elements and their mutual relationships in the limestone. The aim of this paper is also to analyze how significantly the two parameters, silica modulus and lime saturation factor, influence this low grade siliceous limestone sample from the Jayantipuram mine of Andhra Pradesh, India, for the cement making process from the geochemical data.

Key words Jayantipuram mine; limestone; mineralogy; geochemistry; silica modulus

1 Introduction

Limestone, a sedimentary calcareous rock, mostly composed of calcite with some gangue minerals such as quartz, feldspar and mica. The major industries which consume limestone are: cement production, metallurgy (iron and steel making), manufacturing (glass, food processing, paper making, leather, water purification, waste water treatment, flue gas desulphurisation, adhesives, insulation and pH control), agriculture (fertilizers, fungicides, animal feed), and construction (mortar, cement, whitewash, building stone) purposes. Limestone is the lifeline for any cement plant because it constitutes the major raw material component. India is endowed with large deposits of limestone. The estimated total reserves of limestone are 95.623 billion tones. However, the limestone deposits are not uniformly distributed in all the States. There is a concentration of about 73 per cent of the total reserves in five States, namely, Andhra Pradesh, Karnataka, Gujarat, Rajasthan and Madhya Pradesh. This concentration is about 48 per cent in South Zone, 23 per cent in North Zone, 21 per cent in West Zone and the remaining 8 per cent in East Zone (Minerals Year Book, 2006; http://siadipp.nic.in/publicat/cement.htm). For manufacturing of one ton of cement, a quantity of 1.5 ton of limestone is required. Hence, cement plants are necessarily located close to the limestone mines to minimize the transportation cost. The cement grade limestone deposits are depleting day by day because of continuous exploitation of high grade limestone over the years. Hence, many of the cement industries in India are looking for utilization of the existing low grade siliceous limestone from their captive mines for conservation of mineral resources as well as sustaining environment. But, the low grade siliceous limestone can not be used directly as it does not meet the required specifications of cement making. According to Indian cement manufacturers specifications, limestone for cement making, should contain more than 45% CaO; Fe_2O_3 as well as Al_2O_3 1% to 2%; free silica less than 8%; combined Na_2O+K_2O less than 0.6% and P_2O_5 less than 0.6%. Magnesia contents of the limestone should ideally be less

than 3%, although as high as 5% MgO can be used by the cement industry. Magnesia, sulphur and phosphorus are regarded as the most undesirable impurities. The presence of phosphorus (P_2O_5) slows down the setting time of Portland cement (Minerals Year Book, 2006). In order to attain these specifications, low grade siliceous limestone needs to be characterized in terms of their mineralogy and geochemistry.

Portland cement is produced by the high temperature reaction of a lime-bearing material (limestone) with one containing silica, alumina, and ferrous materials. The product, which is known as clinker, has four main compounds—tricalcium silicate (C_3S otherwise known as alite), dicalcium silicate (C_2S otherwise known as belite), calcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF), is afterwards ground with gypsum to give cement. The quality of cement is determined by the composition ratio of these four components. Of these compounds, C_3S and C_3A are mainly responsible for the strength of the cement. High percentage of C_3S (low C_2S) results in high strength, but also high heat generation as the concrete sets. The reverse combination of low C_3S and high C_2S develops strength and generates less heat. C_3A causes undesirable heat and rapid reacting properties, which can be prevented by adding $CaSO_4$ to the final product. C_3A can be converted to more desirable C_4AF by the addition of Fe_2O_3 before heating, but this also inhabits the formation of C_3S. C_4AF makes the cement more resistant to sea water and results in somewhat a slower reaction which evolves less heat. Relatively low grade limestone containing poor CaO can not produce sufficient C_2S and C_3S. Hence, the quality or grade of limestone not only plays an important role in the cost-effectiveness of an integrated cement plant, but also essential for the steady operation of the plant as well as to achieve optimum plant output. Therefore, the constituents such as calcium oxide (CaO), alumina (Al_2O_3), iron oxide (Fe_2O_3) and silica (SiO_2) of the limestone supplied to the plant be within permissible limits of the specifications meant for cement manufacture. It is an established fact that high SiO_2 content in the limestone has an adverse effect on kiln properties and the kiln is one of the most important units for the performance of the cement plant. It is monitored in the form of the silica ratio (SR) which is the ratio between silica and weighted sum of Al_2O_3 and Fe_2O_3. As the silica ratio increases, more heat is required to run the kiln. Nayak and Mallik (2002) have observed that the kiln is more effective where the silica ratio is less than 2.3. The lime saturation factor (LSF): the ratio of CaO and weighted sum of alumina, silica and ferric oxide, is another important parameter that makes a cement plant cost effective. The LSF plays a vital role in cement production because it contains CaO, the primary constituent of cement. It has been found (Ingram and Daugherty, 1991) that kiln operation and cement quality are improved where the CaO in limestone is more than 44%. Thus, both high LSF and a low silica ratio contribute significantly to the cost-effectiveness of a cement plant. To maintain a consistent supply of suitable limestone grades to a cement plant, mineralogical as well as geochemical characterisation of the limestone is essential.

2 Geology of the limestone deposit

The study area is located in the Jayantipuram (16°51′30″N to 16°52′45″N latitude and 80°06′15″E to 80°08′00″E) Village, Jaggayyapeta Taluka of Krishna District, Andhra Pradesh. The Jayantipuram area lies on the northeastern margin of the Palnad sub-basin of Kurnool sedimentary basin overlying the Cuddapah Supergroup of rocks. The Cuddapah Group is in turn deposited over the Achaean basement. The Jayantipuram limestone deposit forms a part of the Nargi Limestone Formation belonging to the Kurnool System. The topography is undulating with surface levels varying from 30 to 73 m above mean sea level. The nearest railway station is Vijayawada and the NH-9 is just 3 kilometres away from the site. A seasonal nalla flowing towards southwest is the major drainage channel in the area.

3 Results and discussion

3.1 Characterization

Petrological studies of the limestone sample from the Jayantipuam area indicated that the sample is dominantly composed of calcite with lesser amounts of quartz, clay and rarely some opaque minerals (mostly pyrite). These limestone rocks have fine- to medium-grained granular mosaics without any fossils. Calcite is generally fine-grained but patches of medium- to coarse-grained anhedral calcite are also common. The medium- to coarse-grained calcite crystals are generally interlocked and contain inclusions of silicates minerals. Quartz occurs in the form of subhedral, medium-grained, and detrital material. The calcite of this limestone deposit

seems to be authigenic in origin and has been precipitated *in-situ*. Micro-fractures filled with fine-grained calcite micro-veins which are considered to be diagenetic. Clay and iron pyrite in trace amounts are present as fine-grained disseminated material in many samples. Rao et al. (2009) studied the siliceous limestone sample from the same area and reported the same mineralogic results for this limestone sample.

X-Ray diffractogram of the sample (Fig. 1) revealed that it contains calcite as the major mineral phase while quartz as the minor silicate gangue mineral. No other mineral phases were observed.

3.2 Geochemistry

The chemistry of the cement in general and Portland cement in particular largely depends upon the geochemistry of its raw materials, i.e., limestone. Approximately 75% of the Portland cement raw material consists of lime (CaO)-bearing material (Lea, 1976). The major and minor elemental chemistry of the randomly hand-picked limestone samples from the Jayantipuram area is presented in Table 1. Chemical analyses revealed that the limestone samples contain lime as the major constituent,

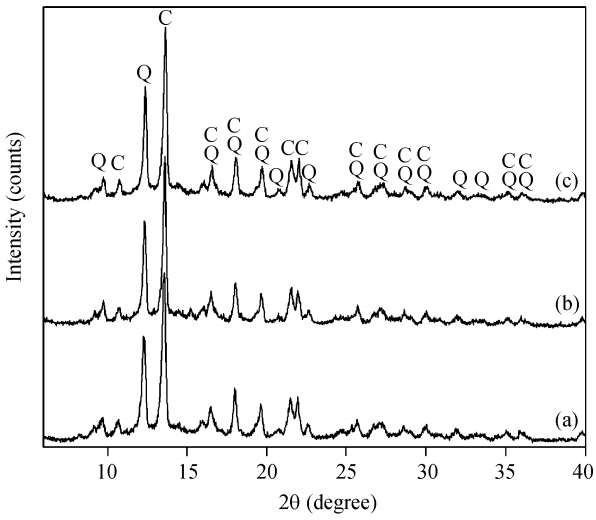

Fig. 1. XRD patterns of three different limestone samples. C. Calcite; Q. quartz.

Table 1 Geochemical characteristics of Jayantipuram limestone samples

Sample No.	LOI	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	MnO_2
1	34.60	17.60	0.88	1.55	43.51	0.46	0.17	0.23	0.03	0.02
2	34.94	18.44	0.61	0.32	44.23	0.15	0.07	0.18	0.03	0.04
3	35.92	14.76	1.59	0.45	45.24	0.64	0.18	0.34	0.05	0.02
4	40.07	7.70	0.53	0.40	49.29	1.30	0.16	0.18	0.02	0.01
5	30.79	27.18	0.96	0.38	38.90	0.42	0.18	0.27	0.03	0.02
6	35.09	17.93	0.50	0.25	44.35	0.35	0.17	0.18	0.02	0.01
7	36.82	14.69	0.82	0.34	46.12	0.49	0.16	0.24	0.03	0.02
8	34.99	16.79	1.33	0.56	44.33	0.52	0.17	0.39	0.04	0.02
9	35.77	16.17	0.58	0.39	45.46	0.53	0.16	0.20	0.02	0.02
10	35.37	16.89	0.74	0.68	44.67	0.42	0.16	0.23	0.03	0.02
11	37.08	13.82	0.68	0.36	46.59	0.47	0.15	0.21	0.02	0.02
12	37.78	11.95	0.87	0.46	47.36	0.59	0.16	0.20	0.03	0.03
13	36.46	15.42	0.64	0.33	45.72	0.38	0.15	0.22	0.02	0.02
14	34.08	20.33	0.94	0.45	42.61	0.61	0.15	0.23	0.04	0.02
15	31.84	26.28	0.53	0.28	39.68	0.41	0.15	0.19	0.02	0.02
16	34.33	18.01	1.54	0.94	43.22	0.62	0.22	0.36	0.07	0.03
17	34.18	18.22	1.54	0.99	42.81	0.65	0.23	0.38	0.07	0.03
18	34.12	18.32	1.66	1.05	42.87	0.74	0.29	0.37	0.08	0.03
19	33.86	18.84	1.77	1.20	42.52	0.67	0.20	0.41	0.09	0.03
20	33.38	19.35	2.00	1.31	41.93	0.75	0.26	0.47	0.11	0.03
21	32.82	19.70	2.16	1.82	41.17	0.87	0.31	0.48	0.14	0.04
22	31.78	21.34	2.27	2.19	40.13	0.84	0.25	0.50	0.16	0.04
23	31.66	21.47	2.02	1.97	39.93	0.77	0.25	0.46	0.15	0.03
24	29.94	24.59	2.00	2.40	37.93	0.83	0.28	0.40	0.15	0.04
25	40.64	6.14	0.49	0.58	50.78	0.48	0.15	0.16	0.03	0.02

followed by Loss on Ignition (LOI) and silica (Table 1). Alumina and iron oxide form the minor constituents while magnesia, alkalis (soda and potash), TiO_2 and MnO_2 are present in traces. SiO_2, Al_2O_3, Fe_2O_3 along with CaO of the limestone form the main ingredients that make up the cement but should be within permissible limits. It is apparent that this siliceous limestone sample can not be used directly for cement industries as the sample contains silica above 8%. LOI of this Jayantipuram mine limestone sample varies from 29.94% to 40.64 %. The LOI content is mostly contributed by the carbonate minerals.

The SiO_2 content in this limestone varies widely, ranging from 6.14% to 27.18%, which is contributed by quartz. The lime content varies between 37.93% to 50.78% and is due to the calcite present in the limestone. The CaO content in this limestone shows a strong positive correlation (Table 2) with that of the LOI (Fig. 2) which may be due to the reason that LOI is contributed mainly by the carbonate content of calcite. CaO shows a very strong negative correlation (Table 2) with that of the silica (Fig. 3). The negative correlation between CaO and SiO_2 is because of the fact that the CaO (from calcite) and SiO_2 (from quartz) are from two different mineral phases and they are not related. Alumina (Al_2O_3) in these samples ranges from 0.49% to 2.27% and shows negative correlation with CaO and positive correlation with iron, magnesium, soda, potash, titania and manganese oxide which could be due to clay material present in the limestone samples. Among other constituents that are commonly important is MgO (0.15% to 1.3%) which might have been derived either from the magnesium-containing skeletal debris or due to post depositional additions or during diagenesis. The chemical composition of the limestone reflects its mineralogical composition.

Table 2 Correlation coefficients of constituents of the limestone sample

	LOI	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	MnO_2
LOI	1.00									
SiO_2	–0.97	1.00								
Al_2O_3	–0.61	0.41	1.00							
Fe_2O_3	–0.59	0.38	0.83	1.00						
CaO	1.00	–0.97	–0.61	–0.59	1.00					
MgO	–0.02	–0.14	0.52	0.49	–0.07	1.00				
Na_2O	–0.53	0.35	0.86	0.79	–0.55	0.61	1.00			
K_2O	–0.61	0.42	0.98	0.78	–0.61	0.49	0.84	1.00		
TiO_2	–0.62	0.42	0.93	0.92	–0.63	0.53	0.84	0.90	1.00	
MnO_2	–0.52	0.38	0.71	0.69	–0.51	0.16	0.52	0.65	0.76	1.00

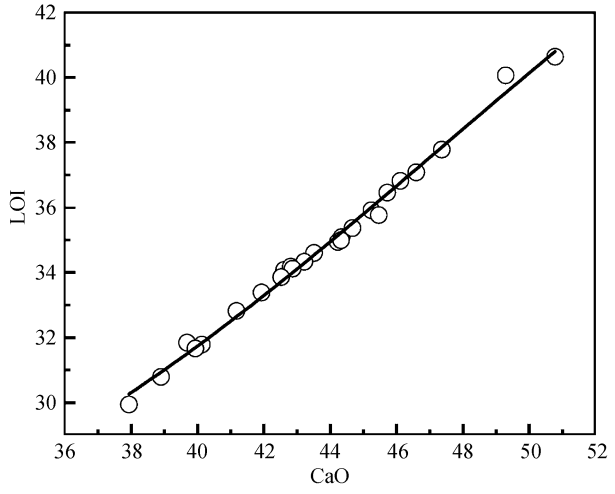

Fig. 2. CaO vs. LOI plotting showing positive correlation.

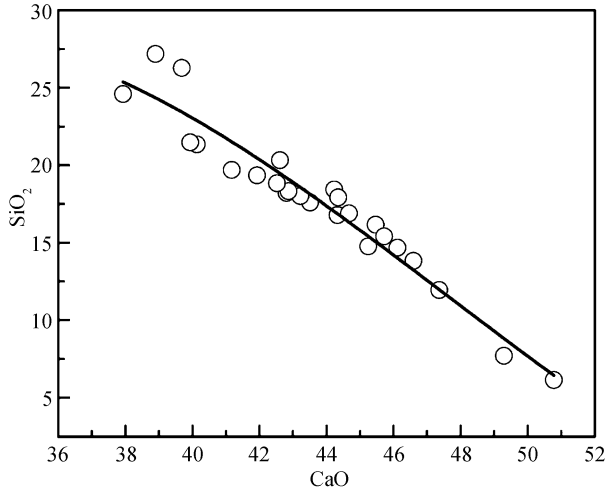

Fig. 3. CaO vs. SiO_2 plotting showing negative correlations.

3.3 Factor analysis

To assist in making geochemical inferences on the origin of the limestone of the Jayantipuram mine, major and minor element data were analyzed using the multivariate factor model of correlation matrix (factor model of Davis, 1973). This was done after standardization, which allowed retention of common factors by minima or inflection points of eigen values (Sahu, 1982). The inflection point methods yielded only two common factors (Table 3) which were varimax rotated to get geochemical interpretations. The first factor could be related with sedimentation and the second factor could be related to diagenesis. The first factor explaining 66.13% of total variances is strongly loaded and can be correlated with the source of the sediments, transportation and deposition. The elements Mg, Na, K, Ti, Mn, Al, and Fe dominantly reflect the clastic sediment contribution. Where as the first factor value shows significant values for minor elements where by they must have been deposited along with carbonate sediments (the 1st factor value; Table 3). Diagenesis is a process by which sedimentary rocks alter after their deposition. Diagenesis takes place either by interaction between their constituents or by reaction between their constituents. Similar is the case for limestones where they undergo some kind of alteration after initial solidification. Diagenesis is anything that happens to a sedimentary rock after original deposition. These alterations include recrystalization, compaction and cementation. All of these things are considered part of the diagenetic process. In general, the nature of end product of diagenesis depends on the composition of original sediments and the physico-chemical processes involved. For carbonate sediments diagenesis is essentially the transformation into a stable calcite phase. This could be the reason why factorial analysis of the geochemical data shows significant factor values (the 2nd factor value; Table 3) of LOI, CaO and SiO_2. LOI and CaO forming calcite by diagenesis.

Table 3 Factor analysis data from geochemistry

	Factor-1	Factor-2	Communality
LOI	–0.32	–0.94	0.98
SiO_2	0.09	0.98	0.96
Al_2O_3	0.90	0.36	0.93
Fe_2O_3	0.84	0.34	0.83
CaO	–0.34	–0.92	0.97
MgO	0.77	–0.32	0.70
Na_2O	0.88	0.25	0.83
K_2O	0.86	0.36	0.88
TiO_2	0.90	0.37	0.95
MnO_2	0.62	0.42	0.56
Eigen value	6.61	1.97	
of trace (%)	66.13	19.72	
Cumulative of trace (%)	66.13	85.85	

3.4 Lime saturation factor

The LSF is a ratio of CaO to the other three main oxides. Applied to clinker, it is calculated as:

$$LSF=CaO/(2.8\ SiO_2 + 1.2\ Al_2O_3 + 0.65\ Fe_2O_3)$$

Often, this is referred to as a percentage and therefore multiplied by 100 and this is mostly applied to clinkers. The lime saturation factor is used for kiln feed control. A higher LSF makes it difficult to burn raw mix. Reactivity of the raw mixture for cement making is influenced greatly in pyrolysis. The pyrolysis characteristics of limestone is greatly influenced by the particle size of calcite crystal, crystal shape that is characteristic of limestone itself and outside impurities such as SiO_2, Al_2O_3 and Fe_2O_3 as well as the existence of state of accompanying minerals (Park et al., 2004). The LSF controls the ratio of alite to belite in the clinker. A clinker with a higher LSF will have a higher proportion of alite to belite than a clinker with a low LSF. Typical LSF values in modern clinkers are 0.92–0.98. Values above 1.0 indicate that free lime is likely to be present in the clinker. This is because, in principle, at LSF=1.0 all the free lime should have combined with belite to form alite. If the LSF is higher than 1.0, the surplus free lime has nothing with which to combine and will remain as free lime. In practice, the mixing of raw materials is never perfect and there are always regions within the clinker where the LSF is locally a little above, or a little below, the target for the clinker as a whole. This means that there is almost always some residual free lime, even where the LSF is considerably below 1.0. It also means that to convert virtually all the belite to alite, an LSF slightly above 1.0 is needed. For the present samples the LSF ranges from 0.5 to 2.8 (Table 4), which indicates that the CaO value is highly erratic and needs to be in uniform range for cement making.

3.5 Silica ratio (SR)

The silica ratio is sometimes called the ‘silica modulus’. The silica modulus has especially great influence

Table 4 Lime saturation factor, alumina ratio and silica modulus data

Sample No.	LSF	SR	AR	Sample No.	LSF	SR	AR
1	0.85	7.24	0.57	14	0.73	14.63	2.09
2	0.84	19.83	1.91	15	0.53	32.44	1.89
3	1.04	7.24	3.53	16	0.82	7.26	1.64
4	2.19	8.28	1.33	17	0.80	7.20	1.56
5	0.50	20.28	2.53	18	0.79	6.76	1.58
6	0.87	23.91	2.00	19	0.76	6.34	1.48
7	1.09	12.66	2.41	20	0.73	5.85	1.53
8	0.91	8.88	2.38	21	0.70	4.95	1.19
9	0.98	16.67	1.49	22	0.63	4.78	1.04
10	0.92	11.89	1.09	23	0.63	5.38	1.03
11	1.17	13.29	1.89	24	0.52	5.59	0.83
12	1.36	8.98	1.89	25	2.80	5.74	0.84
13	1.04	15.90	1.94				

on burning process and on some cement features. The silica ratio is defined as:

$$SR=SiO_2/(Al_2O_3 + Fe_2O_3)$$

Large variation of silica modulus in the clinker can be an indication of poor uniformity in the kiln feed. Changes in coating formation in the burning zone, burnability of the clinker and ring formations with in the kiln can often be traced to changes of silica modulus in the clinker. As a rule, clinker with high silica modulus is more difficult to burn and exhibits poor coating properties. Low silica modulus often leads to ring formations in cement. A high silica ratio means that more calcium silicates are present in the clinker and less aluminate and ferrite. SR is typically between 2.0 and 3.0 for Portland cement clinker. The SR governs the proportion of silicate phases in the clinker. The SR for the present samples ranges from 4.78 to 32.44 (Table 4) which indicate that the samples are higher in SiO_2 content and needs to be brought down to below the specified limits for cement making.

3.6 Alumina ratio (AR)

The alumina ratio is defined as:

$$AR=(Al_2O_3)/(Fe_2O_3)$$

This determines the potential relative proportions of aluminate and ferrite phase in the clinker. An increase in clinker AR (also sometimes written as A/F) means there will be proportionally more aluminate and less ferrite in the clinker. In Ordinary Portland Cement clinker, the AR is usually between 1 and 4. AR approximately equal to 1.4 will be easier to burn if the AR is higher or lower. This is because at an AR of about 1.4, there is more clinker liquid at a lower temperature (Minor constituents such as MgO can alter this optimum AR). The AR for the present samples ranges from 0.57 to 3.53 (Table 4)

4 Implications in cement making

Petrological as well as X-ray diffraction pattern studies indicated that the limestone sample was crystalline and dominantly composed of calcite and quartz. They have a simple mineralogy, and yet they have variable silica and lime contents. CaO with LOI shows strong a positive correlation whereas CaO with SiO_2 shows a strong negative correlation because of mineralogical factors. Silica modulus and lime saturation factor from geochemistry data indicated that the siliceous limestone samples from the Jayantipuram mines of Andhra Pradesh, India, can be utilized for cement making process provided they are processed for beneficiation for silica removal (to less than 8%) to required level where the CaO can be enriched automatically. Hence, in this limestone sample if CaO content is increased to more than 45% and SiO_2 content is decreased below 7%, then the low grade siliceous limestone sample can be utilized for cement making. In such a case the existing low grade siliceous limestone samples, which were considered as waste rock in various limestone mines, can be effectively utilized not only for conservation of mineral resources, but also for sustaining environment. The quality up gradation of limestone can be done by many ways. One alternative is to crush limestone to be -3mm in size and process it in scrubber and classifier, while the other entails grinding of raw feed to less than 200 mesh and carry out beneficiation by froth flotation method (Ananth et al., 1997; Rao et al., 1997; 2009 and 2010) or by column flotation (Vijayakumar et al., 2005).

Acknowledgements The authors are thankful to Director of National Metallurgical Laboratory, Jamshedpur for his valuable guidance, encouragement and permission to publish this work. The authors would like to thank the management of M/s. Madras Cements Limited, Chennai and Ramco Research & Development Centre, Chennai for providing logistic support as well as chemical analysis of the limestone samples, respectively.

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